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910 West Avenue, Austin, Texas 78701 USA

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METHOD FOR PARTIAL HYDROGENATION OF NAPHTHALENE

Inventors:	Dr. Erich Haarer Dr. Alfred Schulz 6700 Ludwigshafen
Applicant:	Badische Anilin- & Soda-Fabrik AG 6700 Ludwigshafen

Notice in accordance with Article 7, § 1 paragraph 2, No. 1 of the law of September 4, 1967 (BGBI. I, p. 960): April 24, 1968

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The partial hydrogenation of polynuclear aromatic compounds on catalysts that consist of copper chromite and larger amounts of alkaline earth oxides is known from German Patent No. 1 094 740. According to US Patent No. 2 475 718, partial hydrogenation of naphthalene can be carried out with Raney alloys in aqueous-alkali solutions or suspensions, but only very pure starting substances can be used and the life-span of the catalysts is low. Further, partial hydrogenation of naphthalene in the presence of compounds of molybdenum and tungsten in a mixture with other catalysts at temperatures between 350 and 800°C is known from US Patent No. 1 960 977 and French Patent No. 667 241. However, at the high temperatures required for this reaction, cyclohexane and decahydronaphthalene arise in large amounts as by-products, and here too the catalysts decline in efficiency after a relatively short time. This is also true for the

catalysts used in accordance with the French Patent No. 38 193 (addition to the said French Patent No. 667 241).

Surprisingly, it has been found that tetrahydronaphthalene is obtained from naphthalene in the presence of catalysts of side groups 6 and 7 of the periodic system while avoiding the said disadvantages if cobalt and nickel molybdate and/or tungstate are used together as catalysts at temperatures of 120-300°C.

An advantage of the new method is that it allows the throughput of larger amounts of substance at higher conversions and therefore gives higher space-time yields than the known methods. Another advantage is the possibility of using lower temperatures, which are milder on the sensitive catalysts as well as the substances being reacted and their reaction products; through this, one achieves, at the same time, a considerably higher catalyst life span, and moreover, an increase of the absolute yields which amount to more, sometimes considerably more, than 90% of theoretical.

The catalysts used in the new method consist of cobalt and nickel molybdate and/or tungstate and, optionally, supports like silica, natural or synthetic silicates, clays or aluminum oxides, among which, above all, the molded articles containing silicic acid are characterized by particularly high stability. Here, molybdenum and tungsten can mutually replace one another completely, but not cobalt and nickel, which must both be present side by side, where the molar ratio can freely vary in a wide range. In general, one uses ratios of 1/4 up to 1.5 mol nickel, preferably from 1/3 up to 1 mol nickel per mol of cobalt in the catalyst. These catalysts can be obtained from the halides, nitrates or oxalates in a substantially known way simply by mixing the components, or even by joint precipitation. If supports are to be used, the supports, optionally after pretreatment by heating to 500-1500°C, can be impregnated with aqueous solutions or suspensions of compounds of the said metals, for example cobalt and nickel ammonium hydroxide, molybdenum or tungstic acid or ammonium molybdate or ammonium tungstate, and then heated to high temperatures, for example 400-600°C; this produces the molybdates or tungstates of the cobalt and nickel. It is advantageous to then subject the catalysts to an additional pretreatment in a reducing medium, for instance with hydrogen or gases that contain hydrogen.

The partial hydrogenation of naphthalene can be undertaken by the new method at relatively low temperatures; in general, the range between 120 and 300°C, especially the range between 180 and 280°C, is chosen. Mainly, the pressure range of 40-300 atm (abs.), preferably 100-250 atm (abs.), is a possibility as the pressure range. The use of solvents is not necessary, but has the advantage that the naphthalene is put completely into solution. Possibilities, among others, are toluene, the xylenes, cumene, cyclohexane, tetrahydronaphthalene, decahydronaphthalene and other cyclic hydrocarbons.

Besides batch methods, especially the continuous methods should be mentioned as advantageous forms of the new method. Those embodiments in which the components of the reaction are quickly mixed with each other, such as the trickle process in liquid phase, have really particular advantages. Here, one can react 1/10 to 1/5 and more parts by volume of a naphthalene solution per part by volume of catalyst per hour, and at the same time operate for months at nearly complete conversion without interrupting or disrupting the reaction.

The parts mentioned in the examples are parts by weight; parts by volume are given as liters per gram.

#### Example 1

800 parts molded silicic acid are held for 4-8 h in the temperature range of 800-1300°C and then impregnated with a solution of 63.6 parts freshly precipitated cobalt hydroxide, 21.2 parts freshly precipitated nickel hydroxide and 233.5 parts ammonium molybdate in 10 wt% aqueous ammonia solution until the entire solution has been absorbed by the support. The catalyst is then heated over 4 h to a temperature of 250°C, and water and ammonia that are present evaporate out and the cobalt and nickel are converted to their molybdates, and it is then treated with hydrogen gas for 10 h at a temperature of 280-310°C at normal pressure.

A solution of 40 parts by weight sulfur-containing raw naphthalene in 120 parts xylene is passed, per hour, over the resulting catalyst at a hydrogen pressure of 200 atm (abs.) and a flow rate of 70 parts by volume hydrogen per hour (converted to normal pressure), where the inlet temperature and the temperature in the reaction vessel are 240-250°C. The reaction product is immediately removed via a cooler, separated from hydrogen by a trap and then the solvent is removed by distillation.

From 40 parts sulfur-containing raw naphthalene, one obtains 40.4 parts (= 98% of theoretical) tetrahydronaphthalene and 0.8 part (= 2% of theoretical) decahydronaphthalene per hour.

#### Example 2

800 parts molded silicic acid, pretreated as in Example 1, is impregnated with a solution of 45.4 parts cobalt hydroxide, 14.8 parts newly precipitated nickel hydroxide, 215 parts ammonium tungstate and about 100 parts ammonia in 1000 parts water until all of the solution has been taken up by the support. After further treatment as in Example 1, the water and ammonia present are evaporated out and the cobalt as well as the nickel are in the form of tungstates. Treatment of the catalyst with hydrogen is also carried out as in Example 1.

The same solution as in Example 1 is passed over the resulting catalyst at the same hourly rate and at hydrogen pressure of 180 atm (abs.) and a flow rate of 60 parts by volume per hour (converted to normal pressure) and a temperature of 245°C.

37.9 parts (= 92% of theoretical) tetrahydronaphthalene and 3.4 parts (= 8% of theoretical) decahydronaphthalene are obtained from the reaction product obtained as in Example 1 and separated from hydrogen and solvents.

### Example 3

The procedure described in Example 1 is followed, but 800 parts silica strands and a solution of 42.2 parts cobalt hydroxide, 42.3 parts nickel hydroxide, 233.5 parts ammonium molybdate and 100 parts ammonia in 1000 parts water are used to make the catalyst, and a temperature of 245°C, a pressure of 150 atm (abs.) and hydrogen flow rate of 100 parts by volume per hour (converted to normal pressure) are used.

39.5 parts (= 96% of theoretical) tetrahydronaphthalene and 1.7 parts (= 4% of theoretical) decahydronaphthalene are obtained from the reaction mixture after separation of the hydrogen and the solvent.

### Claim

A method for hydrogenation of naphthalene to tetrahydronaphthalene in the presence of catalysts that contain metals of the 6th and 7th side groups of the periodic system, which are characterized by the fact that cobalt and nickel molybdate and/or tungstate are used together catalysts at temperatures of 120-300°C.